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(54) Novel zeolite designated CZH-5

(57) A crystalline zeolite, designated as CZH-5, is prepared from organic nitrogen containing cations derived from choline. The zeolite, as synthesized and in anhydrous form, has the following composition expressed as mol ratios of oxides: (0.5 to 1.4) R₂O: (0 to 0.50) M₂O:W₂O₃: xYO₂ where R is an organic nitrogen containing cation derived from choline, x is greater than 5, M is an alkali metal cation, preferably sodium, W is aluminium and/or gallium, preferably aluminium, and Y is silicon and/or germanium, preferably silicon. The CZH-5 zeolite is useful as a catalyst in hydrocarbon conversion processes.

GB 2 079 735 A

SPECIFICATION

Novel zeolite designated CZH-5

5 This invention relates to zeolites having catalytic activity.

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Natural and synthetic aluminosilicates are important and useful compositions having catalytic characteristics. These aluminosilicates are porous and have definite, distinct crystal structures as determined by X-ray diffraction. Within the crystals are a large number of cavities and pores whose dimensions and shapes vary from zeolite to zeolite. Variations in pore dimensions and shapes cause variations in the adsorptive and catalytic properties of the zeolites. Only molecules of certain dimensions and shapes are able to fit into the pores of a particular zeolite while other molecules of large dimensions or different shapes are unable to penetrate the zeolite crystals.

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Because of their unique molecular sieving characteristics as well as their potentially acidic nature, zeolites are especially useful in hydrocarbon processing as adsorbents, and, as catalysts, for cracking, reforming, and other hydrocarbon transformation reactions. Although many different crystalline aluminosilicates have been prepared and tested, the search for new zeolites which can be used in hydrocarbon and chemical processing continues.

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We have discovered a novel family of crystalline aluminosilicate zeolites, hereinafter designated "Zeolite CZH-5" or simply "CZH-5", and a method for their preparation using choline-type compounds. (Choline is trimethyl-(2-hydroxyethyl)ammonium hydroxide).

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In recent years, many crystalline aluminosilicates having desirable adsorption and catalytic properties have been prepared. Typically, zeolites are prepared from reaction mixtures having sources of alkali or alkaline earth metal oxides, silica, alumina, and, optionally, an organic species. However, depending upon the reaction conditions and the composition of the reaction mixture, different zeolites can be formed even if the same organic species is used. For example, zeolites, ZK-4, ZSM-4, faujasite and PHI, have been prepared from tetramethylammonium compounds; and zeolites ZK-5 and ZSM-10 have been prepared from N,N'-dimethyltriethylenediammonium compounds.

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U.S. 4,046,895, discloses the preparation of a new family of crystalline zeolites called "ZSM-21". One member of the ZSM-21 family, ZSM-38, is described as having a composition in terms of mol ratios of oxides, in the anhydrous state, of $(0.3 \text{ to } 2.5) \text{ R}_2\text{O} : (0 \text{ to } 0.8) \text{ M}_2\text{O} : \text{Al}_2\text{O}_3 : (\text{greater than } 8) \text{ SiO}_2$, wherein R is derived from trialkyl(2-hydroxyalkyl) ammonium compounds, such as choline, and M is an alkali metal cation.

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U.S. 4,086,186 and U.S. 4,116,813 disclose the preparation of a crystalline zeolite called ZSM-34, which has the composition as synthesized, and in anhydrous form, expressed as mol ratios of oxides as follows: $(0.5 \text{ to } 1.3) \text{ R}_2\text{O} : (0 \text{ to } 0.15) \text{ Na}_2\text{O} : (0.10 \text{ to } 0.50) \text{ K}_2\text{O} : \text{Al}_2\text{O}_3 : x \text{ SiO}_2$ where R is an organic nitrogen-containing cation derived from choline and x is 8 to 50.

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U.S. 4,187,283, discloses the preparation of a crystalline zeolite called ZSM-47. ZSM-47 is disclosed as having been prepared from a 2-(hydroxyalkyl)trialkylammonium compound such as choline.

Although ZSM-47, ZSM-34 and ZSM-38 are taught by the art as being prepared from choline, they are recognized as having different crystal structures and catalytic capabilities. The new zeolite CZH-5 has a still different crystal structure from ZSM-34, ZSM-38 and ZSM-47, as shown by its different X-ray diffraction pattern. It also has different catalytic capabilities.

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The present invention is a zeolite having a mol ratio of an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, and mixtures thereof greater than about 5:1 and having the X-ray diffraction lines of Table I. The zeolite further has a composition, as synthesized and in the anhydrous state, in terms of mol ratios of oxides as follows. $(0.5 \text{ to } 1.4) \text{ R}_2\text{O} : (0 \text{ to } 0.50) \text{ M}_2\text{O} : \text{W}_2\text{O}_3 : (\text{greater than } 5) \text{ YO}_2$ wherein M is an alkali metal cation, W is selected from aluminum, gallium, and mixtures thereof, Y is selected from silicon, germanium and mixtures thereof, and R is a cation derived from a choline-type compound. CZH-5 zeolites can have a $\text{YO}_2 : \text{W}_2\text{O}_3$ mol ratio greater than about 5:1, preferably greater than about 40:1. The range of $\text{YO}_2 : \text{W}_2\text{O}_3$ mol ratios is preferably from about 8:1 to 150:1, more preferably from about 10:1 to 100:1, and most preferably from about 40:1 to about 100:1. Preferably, CZH-5 is an aluminosilicate wherein W is aluminum and Y is silicon.

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The present invention also involves a method for preparing CZH-5 zeolites, comprising preparing an aqueous mixture containing sources of an organic nitrogen-containing compound, an oxide selected from aluminum oxide, gallium oxide, and mixtures thereof, and an oxide selected from silicon oxide, germanium oxide, and mixtures thereof, and having a composition, in terms of mol ratios of oxides, falling within the following ranges: $\text{YO}_2 / \text{W}_2\text{O}_3$, 5:1 to 350:1, $\text{R}_2\text{O} / \text{W}_2\text{O}_3$, 0.5:1 to 40:1, wherein Y is selected from silicon, germanium, and mixtures thereof, W is selected from aluminum, gallium and mixtures thereof, and R is a cation derived from a choline-type compound; maintaining the mixture at a temperature of at least 100°C until the crystals of said zeolite are formed; and recovering said crystals.

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CZH-5 zeolites have a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines:

TABLE I

	d(A)	Intensity	
5	11.85 ± 0.10	S	5
	11.60 ± 0.10	M	
	9.97 ± 0.05	M	
	4.25 ± 0.02	VS	
	3.87 ± 0.01	M	
10	3.83 ± 0.01	M	10
	3.46 ± 0.01	M	

A typical CZH-5 aluminosilicate zeolite has the X-ray diffraction pattern of Table II.

TABLE II

	2θ	d(A)	I/I ₀	
15	7.46	11.85	50	15
	7.63	11.60	30	
20	8.87	9.97	25	20
	14.78	5.99	3	
	15.25	5.81	4	
	18.74	4.73	14	
25	18.95	4.68	5	25
	19.15	4.63	8	
	20.06	4.43	5	
	20.92	4.37	3	
	21.32	4.25	100	
30	21.77	4.08	14	30
	21.87	4.06	7	
	21.98	4.04	15	
	22.47	3.96	6	
	22.96	3.87	37	
35	23.19	3.83	28	35
	23.83	3.73	3	
	24.47	3.64	3	
	25.19	3.54	6	
	25.77	3.46	16	
40	26.30	3.39	11	40
	26.80	3.33	13	
	26.94	3.31	5	
	27.98	3.19	7	
	28.84	3.14	3	
45	29.30	3.05	5	45
	30.75	2.91	3	
	30.93	2.89	6	

These values were determined by standard techniques. The radiation was the K-alpha/doublet of copper and a scintillation counter spectrometer with a stripchart pen recorder was used. The peak heights I and the positions, as a function of 2θ where θ is the Bragg angle, were read from the spectrometer chart. From these measured values, the relative intensities, 100I/I₀, where I₀ is the intensity of the strongest line or peak, and d, the interplanar spacing in Angstroms corresponding to the recorded lines, were calculated. The X-ray diffraction pattern of Table I is characteristic of all species of CZH-5 family compositions. The zeolite produced by exchanging the metal or other cations present in the zeolite with various other cations yields substantially the same diffraction pattern although there can be minor shifts in interplanar spacing and variations in relative intensity. Minor variations in the diffraction pattern can also result from variations in the choline-type compound used in the preparation and from variations in the silica-to-alumina mol ratio of a particular sample. Calcination can also cause minor shifts in the X-ray diffraction pattern. Notwithstanding these minor perturbations, the basic crystal lattice structure remains unchanged.

CZH-5 zeolites can be suitably prepared from an aqueous solution containing sources of an alkali metal oxide, a choline-type compound, an oxide of aluminum or gallium, or mixture of the two, and an oxide of silicon or germanium, or mixture of the two. The reaction mixture should have a composition in terms of

	Broad	Preferred	
	$\text{YO}_2/\text{W}_2\text{O}_3$	5-350	12-200
	$\text{M}_2\text{O}/\text{W}_2\text{O}_3$	0.5-20	1-17
5	$\text{R}_2\text{O}/\text{W}_2\text{O}_3$	0.5-40	5-25
	$\text{MCl}/\text{W}_2\text{O}_3$	20-200	50-150
	$\text{H}_2\text{O}/\text{W}_2\text{O}_3$	500-20000	1500-15000
			5

wherein R is as disclosed above, Y is silicon, germanium or both, and W is aluminum, gallium or both. M is
 10 an alkali metal, preferably sodium. Typically, an alkali metal hydroxide or alkali metal halide is used in the
 reaction mixture; however, these components can be omitted so long as the equivalent basicity is
 maintained. The choline-type compound can provide hydroxide ion. 10

By "choline-type compound" is meant an organic nitrogen compound having the formula $\text{R}^1\text{R}^2\text{R}^3\text{NR}^4\text{OH}-$
 X. R^1 , R^2 and R^3 are C_1 to C_4 lower alkyl; R^4 is C_1 to C_5 alkyl and X is an anion. The choline-type compounds
 15 are generally trialkyl (2-hydroxyalkyl)ammonium compounds. The preferred choline-type compound has the
 choline (or trimethyl(2-hydroxyethyl)ammonium) cation. The choline-type compound can be in the form of
 the hydroxide, e.g., choline hydroxide, the halide, e.g., choline chloride, bromide, or fluoride, or it can be
 associated with other suitable anions such as sulfates, acetates, and nitrates. The reaction mixture which
 allows the synthesis of CZH-5 is typically prepared by the addition to water of choline chloride, choline
 20 fluoride, choline hydroxide, or mixtures of these and other choline-type compounds. 20

The reaction mixture is prepared using standard zeolitic preparation techniques. Typical sources of
 aluminum oxide for the reaction mixture include aluminates, alumina, and aluminium compounds such as
 AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$. Typical sources of silicon oxide include silicates, silica hydrogel, silicic acid, colloidal
 silica, and silica hydroxides. Gallium and germanium can be added in forms corresponding to their
 25 aluminum and silicon counterparts. 25

Salts, particularly alkali metal halides such as sodium chloride, can be added to or formed in the reaction
 mixture. They facilitate the crystallization of the zeolite and prevent silica occlusion in the lattice, as disclosed
 in U.S. 3,849,463.

The reaction mixture is maintained at an elevated temperature until the crystals of the zeolite are formed.
 30 The temperatures during the hydrothermal crystallization step are typically maintained at a temperature of
 from about 100°C to about 235°C , preferably from about 120°C to about 200°C and most preferably from
 about 135°C to about 165°C . The crystallization period is typically greater than 3 days and preferably from
 about 7 days to about 50 days. 30

The hydrothermal crystallization is conducted under pressure and usually in an autoclave so that the
 35 reaction mixture is subject to autogenous pressure. Although the reaction mixture can be stirred during
 crystallization, preferably it is not. 35

Once the zeolite crystals have formed, the solid product is separated from the reaction mixture by standard
 mechanical separation techniques such as filtration. The crystals are water-washed and then dried, e.g., at
 90 - 150°C for from 8 to 24 hours, to obtain the as synthesized, CZH-5 zeolite crystals. The drying step can be
 40 performed at atmospheric or subatmospheric pressures. 40

During the hydrothermal crystallization step, the CZH-5 crystals can be allowed to nucleate spontaneously
 from the reaction mixture. The reaction mixture can also be seeded with CZH-5 crystals both to direct, and
 accelerate the crystallization, as well as to minimize the formation of undesired aluminosilicate
 contaminants. If the reaction mixture is seeded with CZH-5 crystals, the concentration of the choline-type
 45 organic nitrogen compound can be greatly reduced or eliminated, but it is preferred to have some organic
 compound present, e.g. an alcohol. 45

The synthetic CZH-5 zeolites can be used as synthesized or can be thermally treated (calcined). Usually, it
 is desirable to remove the alkali metal cation by ion exchange and replace it with hydrogen, ammonium, or
 any desired metal ion. The zeolite can be used in intimate combination with hydrogenating components,
 50 such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble
 metal, such as palladium or platinum, for those applications in which a hydrogenation-dehydrogenation
 function is desired. Typical replacing cations can include metal cations, e.g., rare earth, Group IIA and Group
 VIII metals, as well as their mixtures. Of the replacing metallic cations, cations of metals such as rare earth,
 Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co are particularly preferred. 50

The hydrogen, ammonium, and metal components can be exchanged into the zeolite. The zeolite can also
 be impregnated with the metals, or, the metals can be physically intimately admixed with the zeolite using
 standard methods known to the art. And, the metals can be occluded in the crystal lattice by having the
 desired metals present as ions in the reaction mixture from which the CZH-5 zeolite is prepared. 55

Typical ion exchange techniques involve contacting the synthetic zeolite with a solution containing a salt
 60 of the desired replacing cation or cations. Although a wide variety of salts can be employed, chlorides and
 other halides, nitrates, and sulfates are particularly preferred. Representative ion-exchange techniques are
 disclosed in a wide variety of patents including U.S. Patent Nos. 3,140,249; 3,140,251; and 3,140,253. 60

calcined in air or inert gas at temperatures ranging from about 200°C to 820°C for periods of time ranging from 1 to 48 hours, or more, to produce a catalytically-active product especially useful in hydrocarbon conversion processes.

Regardless of the cations present in the synthesized form of the zeolite, the spatial arrangement of the atoms which form the basic crystal lattice of the zeolite remains essentially unchanged. The exchange of cations has little, if any, effect on the zeolite lattice structures.

The CZH-5 aluminosilicate can be manufactured into a wide variety of physical forms. Generally speaking, the zeolite can be in the form of a powder, a granule, or a molded product, such as extrudate having particle size sufficient to pass through a 2-mesh (Tyler) screen and be retained on a 400-mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion with an organic binder, the aluminosilicate can be extruded before drying, or, dried or partially dried and then extruded.

The zeolite can be composited with other materials resistant to the temperatures and other conditions employed in organic conversion processes. Such matrix materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Use of a material in conjunction with the synthetic zeolite, i.e., combined therewith, which is active, tends to improve the conversion and selectivity of the catalyst in certain organic conversion processes. Inactive materials suitably serve as diluents to control the amount of conversion in a given process so that products can be obtained economically without employing other means for controlling the rate of reaction. Frequently, zeolite materials have been incorporated into naturally occurring clays, e.g., bentonite and kaolin. These materials, i.e., clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable to provide a catalyst having good crush strength, because in petroleum refining the catalyst is often subjected to rough handling. This tends to break the catalyst down into powder-like materials which cause problems in processing.

Naturally occurring clays which can be composited with the synthetic zeolites of this invention include the montmorillonite and kaolin families, which families include the sub-bentonites, and the kaolins commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Fibrous clays such as sepiolite and attapulgite can also be used as supports. Such clays can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification.

In addition to the foregoing materials, the CZH-5 zeolites can be composited with porous matrix materials and mixtures of matrix materials such as silica, alumina, titania, magnesia, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania, titania-zirconia as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia. The matrix can be in the form of a cogel.

The CZH-5 zeolites can also be composited with other zeolites such as synthetic and natural faujasites, (e.g. X and Y) erionites, and mordenites. They can also be composited with purely synthetic zeolites such as those of the ZSM series. The combination of zeolites can also be composited in a porous inorganic matrix.

The relative proportions of the crystalline aluminosilicate zeolite of this invention and inorganic oxide gel matrix can vary widely. The CZH-5 content can range from about 1 to about 90 percent by weight but is more usually in the range of about 2 to about 50 percent by weight of the composite.

The following examples illustrate the preparation of CZH-5 through hydrothermal crystallization.

Example 1

In a 500 ml Teflon (Registered Trade Mark) bottle 0.2902 grams of sodium aluminate (48% Al_2O_3 , 33% Na_2O) 12.46 grams choline chloride and 50 grams of water were mixed. To this mixture was added a second solution prepared by dissolving 6.65 grams sodium chloride in 100 grams of distilled water.

To the solutions so prepared, a third solution comprising N-sodium silicate solution (28% SiO_2), 46.34 grams, in 150 grams distilled water was added. The final reaction mixture was obtained by adding a hydrochloric acid solution prepared by the mixture of 2.68 grams of concentrated HCl (36% HCl) in 71.88 grams distilled water.

The Teflon reaction bottle was sealed and the reaction mixture was autoclaved in an oven at 150°C for 15 days until the crystalline precipitate was formed.

The crystals were allowed to settle, the clear supernatant liquid was decanted and the crystals were filtered, washed with distilled water to remove chloride ions and dried for 16 hours at 120°C and 20 inches of vacuum under nitrogen. The X-ray diffraction pattern of the product was taken and was found to be that of Table III which is characteristic of CZH-5.

TABLE III

	d(A)	Intensity	
5	11.79	S	5
	11.56	M	
	9.94	M	
	5.97	W	
	5.79	W	
10	4.72	W	10
	4.67	W	
	4.62	W	
	4.42	W	
	4.24	VS	
15	4.07	VS	15
	4.04	S	
	3.96	W	
	3.87	M	
	3.82	M	
20	3.72	W	20
	3.63	W	
	3.53	W	
	3.45	M	
	3.38	W	
25	3.32	W	25
	3.18	W	
	3.13	W	
	3.04	W	
	2.91	W	
30	2.88	W	30

Example 2

In a 500 ml Teflon bottle 0.5743 grams of sodium aluminate (48% Al_2O_3 , 33% Na_2O) 12.33 grams choline chloride and 50 grams of water were mixed. To this mixture was added a second solution prepared by dissolving 6.54 grams sodium chloride in 100 grams of distilled water.

To the solution so prepared, a third solution comprising N-sodium silicate solution (28% SiO_2), 45.86 grams, in 150 grams distilled water was added. The final reaction mixture was obtained by adding a hydrochloric acid solution prepared by the mixture of 2.96 grams of concentrated HCl (36% HCl) in 72.0 grams distilled water.

The Teflon reaction bottle was sealed and the reaction mixture was autoclaved in an oven at 150°C for 15 days until the crystalline precipitate was formed.

The crystals were allowed to settle, the clear supernatant liquid was decanted and the crystals were filtered, washed with distilled water to remove chloride ions and dried for 16 hours at 120°C and 20 inches of vacuum under nitrogen. The X-ray diffraction pattern of the product was taken and was found to be that of Table IV, typical of the CZH-5 zeolite.

TABLE IV

	d(A)	Intensity	
5	11.79	S	5
	11.56	M	
	9.94	M	
	5.97	W	
	5.79	W	
10	4.72	M-W	10
	4.67	W	
	4.62	W	
	4.42	W	
	4.24	S	
15	4.07	M	15
	4.04	M	
	3.96	W	
	3.87	S	
	3.82	S	
20	3.72	W	20
	3.63	W	
	3.53	W	
	3.45	M	
	3.38	M	
25	3.32	M	25
	3.18	W	
	3.13	W	
	3.04	W	
	2.91	W	
30	2.88	W	30

Examples 3-7

Examples 3-7 illustrate the preparation of CZH-5 and the effect of the length of time the reaction mixture is maintained at elevated temperature and autogenous pressure on the formation of the zeolite crystals.

35 The reaction mixtures for examples 3-7 were prepared to have the following mol ratios of ingredients: 35

40	SiO ₂ /Al ₂ O ₃	80:1	40
	R ₂ O/Al ₂ O ₃	16:1 (R=choline)	
	Na ₂ O/Al ₂ O ₃	4.0:1	
	H ₂ O/Al ₂ O ₃	8328:1	
	NaCl/Al ₂ O ₃	84:1	
	wt % Al ₂ O ₃ and SiO ₂	3	
	wt% NaCl	3	

45 For each of the experiments of examples 3 to 7 the reaction mixture was maintained at 150°C under autogenous pressure without stirring during crystallization. 45

Table V presents the crystallization time and the results of the analysis of the products produced.

TABLE V

	Example	3	4	5	6	7	
5	Crystallization Time (days)	3	7	13	15	16	5
	Prod. Analyses: Structure (XRD)	amor	50%CZH-5	75%CZH-5	100%CZH-5	100%CZH-5	
10	Composition						10
	LOI*	6.68	8.05	3.03	4.33	8.96	
15	SiO ₂ /Al ₂ O ₃	37.5	42.5	53.7	64.2	54.2	15
	R ₂ O/Al ₂ O ₃	1.02	1.08	1.33	1.38	1.33	
	Na ₂ O/Al ₂ O ₃	.28	.23	.17	.20	.23	

* loss on ignition - 540°C, 10 hours, in air.

CZH-5 zeolites are useful in hydrocarbon conversion reactions. Hydrocarbon conversion reactions are chemical and catalytic processes in which carbon containing compounds are changed to different carbon containing compounds. Examples of hydrocarbon conversion reactions include catalytic cracking, hydrocracking, and olefin and aromatics formation reactions. The catalysts are useful in other petroleum refining and hydrocarbon conversion reactions such as isomerizing n-paraffins and naphthenes, polymerizing and oligomerizing olefinic or acetylenic compounds such as isobutylene and butene-1, reforming, alkylating, isomerizing polyalkyl substituted aromatics (e.g., ortho xylene), and disproportionating aromatics (e.g., toluene) to provide a mixture of benzene, xylenes and higher methylbenzenes. The CZH-5 catalysts have high selectivity, and under hydrocarbon conversion conditions can provide a high percentage of desired products relative to total products.

CZH-5 zeolites can be used in processing hydrocarbonaceous feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds and can be from many different sources, e.g., virgin petroleum fractions, recycle petroleum fractions, shale oil, liquefied coal, tar sand oil, and in general any carbon containing fluid susceptible to zeolitic catalytic reactions. Depending on the type of processing the hydrocarbonaceous feed is to undergo, the feed can be metal containing or without metals, it can also have high or low nitrogen or sulfur impurities. It can be appreciated, however, that in general the processing will be more efficient (and the catalyst more active) the lower the metal, nitrogen or sulfur content of the feedstock.

The conversion of hydrocarbonaceous feeds can take place in any convenient mode, for example, in fluidized bed, moving bed, or fixed bed reactors depending on the types of process desired. The formulation of the catalyst particles will vary depending on the conversion process and method of operation.

Using CZH-5 catalysts containing hydrogenation components, heavy petroleum residual stocks, cyclic stocks, and other hydrocrackable charge stocks can be hydrocracked at temperatures from 175°C to 485°C using molar ratios of hydrogen to hydrocarbon charge from 1 to 100. The pressure can vary from 0.5 to 350 bar and the liquid hourly space velocity from 0.1 to 30. For these purposes, the CZH-5 catalyst can be composited with mixtures of inorganic oxide supports as well as with faujasites such as X and Y.

Hydrocarbon cracking stocks can be catalytically cracked using CZH-5 at liquid hourly space velocities from 0.5 to 50, temperatures from about 260°C to 625°C, and pressures from subatmospheric to several hundred atmospheres.

CZH-5 can be used to dewax hydrocarbonaceous feeds by selectively removing straight chain and slightly branched chain paraffins. The process conditions can be those of hydrodewaxing - a mild hydrocracking, or they can be at lower pressures in the absence of hydrogen. Dewaxing in the absence of hydrogen at pressures less than 30 bar, and preferably less than 15 bar, is preferred as significant amounts of olefins can be obtained from the cracked paraffins.

CZH-5 can also be used in reforming reactions using temperatures from 300°F to 600°C, pressures from 35 to 110 bar, and liquid hourly space velocities from 0.1 to 20. The hydrogen to hydrocarbon mol ratio can be generally from 1 to 20.

The catalyst can also be used to hydroisomerize normal paraffins, when provided with a hydrogenation component, e.g., platinum. Hydroisomerization is carried out at temperatures from 90 to 375°C, and liquid hourly space velocities from 0.01 and 5. The hydrogen to hydrocarbon mol ratio is typically from 1:1 to 5:1. Additionally, the catalyst can be used to isomerize and polymerize olefins using temperatures from 0°C to

reactions.

CZH-5 can be used in hydrocarbon conversion reactions with active or inactive supports, with organic or inorganic binders, and with and without added metals. These reactions are well known to the art as are the reaction conditions. CZH-5 can also be used as an adsorbent for hydrocarbonaceous fluids.

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CLAIMS

1. A zeolite designated CZH-5 having a mol ratio of an oxide selected from silicon oxide, germanium oxide and mixtures thereof to an oxide selected from aluminium oxide, gallium oxide, and mixtures thereof greater than 5:1, and having the X-ray diffraction lines referred to in the foregoing Table I. 10
2. A zeolite designated CZH-5 having a composition, as synthesized and in the anhydrous state, in terms of mol ratios of oxides as follows: $(0.5 \text{ to } 1.4)R_2O:(0 \text{ to } 0.50)M_2O:W_2O_3:(\text{greater than } 5)YO_2$ wherein M is an alkali metal cation, W is selected from aluminium, gallium and mixtures thereof, Y is selected from silicon, germanium and mixtures thereof, and R is a cation derived from a choline type compound, and having the X-ray diffraction lines referred to in the foregoing Table I. 15
3. A zeolite as claimed in Claim 2, wherein the $YO_2:W_2O_3$ mol ratio is in the range from 8:1 to 150:1.
4. A zeolite as claimed in Claim 3, wherein said mol ratio is in the range from 10:1 to 100:1.
5. A zeolite as claimed in Claim 4, wherein said mol ratio is in the range from 40:1 to 100:1.
6. A zeolite as claimed in any one of Claims 2 to 5, wherein M is sodium, W is aluminium and Y is silicon.
7. A zeolite as claimed in any preceding claim, wherein the zeolite has undergone ion exchange with hydrogen, ammonium, rare earth metal, Group IIA metal, or Group VIII metal ions. 20
8. A zeolite as claimed in any one of Claims 1 to 6, wherein one or more rare earth metals, Groups IIA metals, or Group VIII metals are occluded in the zeolite.
9. A zeolite as claimed in any preceding claim, wherein the zeolite has been thermally treated at a temperature in the range from 200 to 820°C. 25
10. A zeolite composition comprising a zeolite as claimed in any preceding claim and in association therewith an inorganic matrix.
11. A method of preparing a CZH-5 zeolite as claimed in Claim 1, comprising:
 - (a) preparing an aqueous mixture containing sources of a choline-type compound, an oxide selected from aluminium oxide, gallium oxide, and mixtures thereof, and an oxide selected from silicon oxide, germanium oxide, and mixtures thereof; 30
 - (b) maintaining the mixture at a temperature of at least 100°C until the crystals of said zeolite form; and
 - (c) recovering said crystals.
12. A method according to Claim 11, wherein the aqueous mixture has a composition in terms of mol ratios of oxides falling within the ranges: $YO_2:W_2O_3$, 5:1 to 350:1; and $R_2O:W_2O_3$, 0.5:1 to 40:1; wherein Y is selected from silicon, germanium and mixtures thereof, W is selected from aluminium, gallium, and mixtures thereof, and R is a cation derived from a choline-type compound. 35
13. A method according to Claim 11 or 12, wherein the temperature of step (b) is from 135 to 175°C and the mixture is maintained at said temperature under autogenous pressure.
14. A method of preparing a CZH-5 zeolite substantially as described in any one of the foregoing Examples. 40
15. A CZH-5 zeolite whenever prepared by the method claimed in any one of Claims 11 to 14.
16. A hydrocarbon conversion process comprising contacting a hydrocarbonaceous feed with a CZH-5 zeolite as claimed in any one of Claims 1 to 9 and 15 under hydrocarbon conversion conditions.
17. A hydrocarbon conversion process according to Claim 16, wherein the CZH-5 zeolite is in the form of a composition as claimed in Claim 10. 45
18. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is hydrocracking.
19. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is dewaxing.
20. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is reforming. 50
21. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is olefin polymerization or oligomerization.
22. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is isomerization.
23. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is disproportionation. 55
24. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is alkylation.
25. A hydrocarbon conversion process according to Claim 16 or 17, wherein said process is catalytic cracking.

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